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Reprint of: Infrared chemiluminescence study of the reaction Cl + HI → HCl + I at enhanced collision energies

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ABSTRACT

The detailed rate constant $k(V',R',T';T)$, where V', R' and T' are product vibrational, rotational and translational energies, and T is the reagent translational energy (approximately 4.7–12 kcal mole^{-1}), has been measured for Cl + HI → HCl + I by the infrared chemiluminescence method. The main findings are (a) that T becomes principally T', (b) that V' broadens in distribution and (c) a *second* peak appears in R' of $v' = 4$, at enhanced T.

1. Experimental

In earlier infrared chemiluminescence studies of the reaction [1–4] $Cl + HI \rightarrow HCl + I$ ($-\Delta H_0^0 = 31.7$ kcal mole^{-1}), and some related studies (e.g. Refs. [5,6]), we have made use of the arrested relaxation variant of the infrared chemiluminescence method to obtain detailed rate constants $k(V',R',T')$, in which V',R' and T' are the product vibrational, rotational and translational energies. The reagents have always been in a room-temperature thermal distribution. (We symbolise the temperature as T_K.) This has meant that the mean collision energy (reagent translational energy; T) has been $T \approx E_a + \frac{3}{2}RT_K$ [7]; $\therefore T \approx 1.5$ kcal mole^{-1}.

We have now (for the first time) made the collision energy a variable in infrared chemiluminescence experiments, by a modification of the inlet system for tie two reagents. Previously this has been a pair of effusive nozzles, i.e. uncollimated room temperature thermal beams [1,6]. This has been altered to either (a) a supersonic jet directed across a (room-temperature) effusive nozzle, or (b) a pair of supersonic jets (Table 1). The kinematics of Cl + HI (large mass of HI) made the single jet arrangement acceptable. Three experiments were performed using a single-jet crossing an uncollimated effusive beam at a point about 20 mm from the jet orifice. Comparing head-on with head-to-tail collisions the spread in T for this arrangement was 4.7 ± 1.7, 6 ± 2.3 and 12 ± 3.5 kcal mole^{-1}. Two further experiments at $T \approx 6$ kcal mole^{-1} have also been performed employing a pair of supersonic jets, for which the spread in T will be somewhat less. The jets crossed at a point approximately 10 mm from the pair of graphite ovens from which they issued (hot oven for Cl_2 + Cl, cold for HI). The populations in $v' = 4$ from these twin-jet experiments at $T \approx 6$ were 30% lower than that from the jet + effusive beam. The source of this difference is unclear; possibly there is more reaction with a collision energy in excess of the mean value for the jet + thermal beam geometry. There was no significant difference between the initial rotational distributions of the HCl product for the twin-jet and the jet + beam experiments.

Since none of these experiments was performed under single-collision conditions, some reaction must have occurred in secondary collisions of the Cl at less than the calculated primary collision energy. The experiments did, however, provide an internal check on the fact that the calculated T was indeed the actual T for a significant fraction of the reactive collisions, since the reaction was found to populate vibrational–rotational states up to an energy of 38 kcal for a (calculated) $T = 4.7$ kcal mole^{-1}, up to 40 kcal for $T = 6$ kcal mole^{-1}, and up to 46 kcal for $T = 12$ kcal mole^{-1}. These figures for $(V' + R')_{max}$ are in every case 1–2 kcal mole^{-1} in excess of the *mean* total available energy. An important component of the mean total available energy, E'_{tot}, is the mean collision energy T, since

$$E'_{tot} = -\Delta H_0^0 + T + RT_K, \quad (1)$$

where the final term represents the mean rotational energy in the reagents. This equation is based on the analogous expression $E'_{tot} = -\Delta H_0^0 + E_a + \frac{3}{2}RT_K + RT_K$ which has been successful in predicting the total energy available from thermal reactions [3–6]; in this expression $E_a + \frac{3}{2}RT_K$ is the mean collision energy of reacting molecules [7].

In all experiments chlorine atoms were formed by thermal dissociation of Cl_2 in an oven consisting of a hollow cylindrical graphite rod, heated by a 100–150 amp current. There was a circular orifice mid-way along the length of the oven. Orifice diameters, oven pressures and temperatures are listed in Table 1. Typically (200 torr, 1700 °K) the Cl_2 was ≈15% dissociated. The translational energy of Cl was calculated (naively) assuming that the Cl/Cl_2 mix-

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Table 1
Experimental conditions for the 5 experiments performed.

	T (kcal mole^{-1})	Apparatus	Cl_2 Oven temp. (°K)	Cl_2 Oven pressure (torr)	Cl_2 Orifice diameter (mm)	FIOWS (μmole sec^{-1})	Background pressure (torr)
1	4.7[a]	2	1380	19	1.00	30 $Cl_2$100 HI	2×10^{-5}
2	6.5[b]	1	1690	175	0.33	36 Cl_2 65 HI	1×10^{-5}
3	6.4[b]	2	1700	230	0.56	50 Cl_2 50 HI	1×10^{-5}
4	5.7[a]	2	1650	175	0.22	46 Cl_2 120 HI	$2–3 \times 10^{-5}$
5	12.1[a]	2	1700	260	0.22[c]	43 Cl_2 84 He 180 HI	4×10^{-5}

[a] Experiments using a single supersonic jet.
[b] Experiments using two jets.
[c] 2 orifices of this diameter side by side in the same oven (≈2 mm apart).

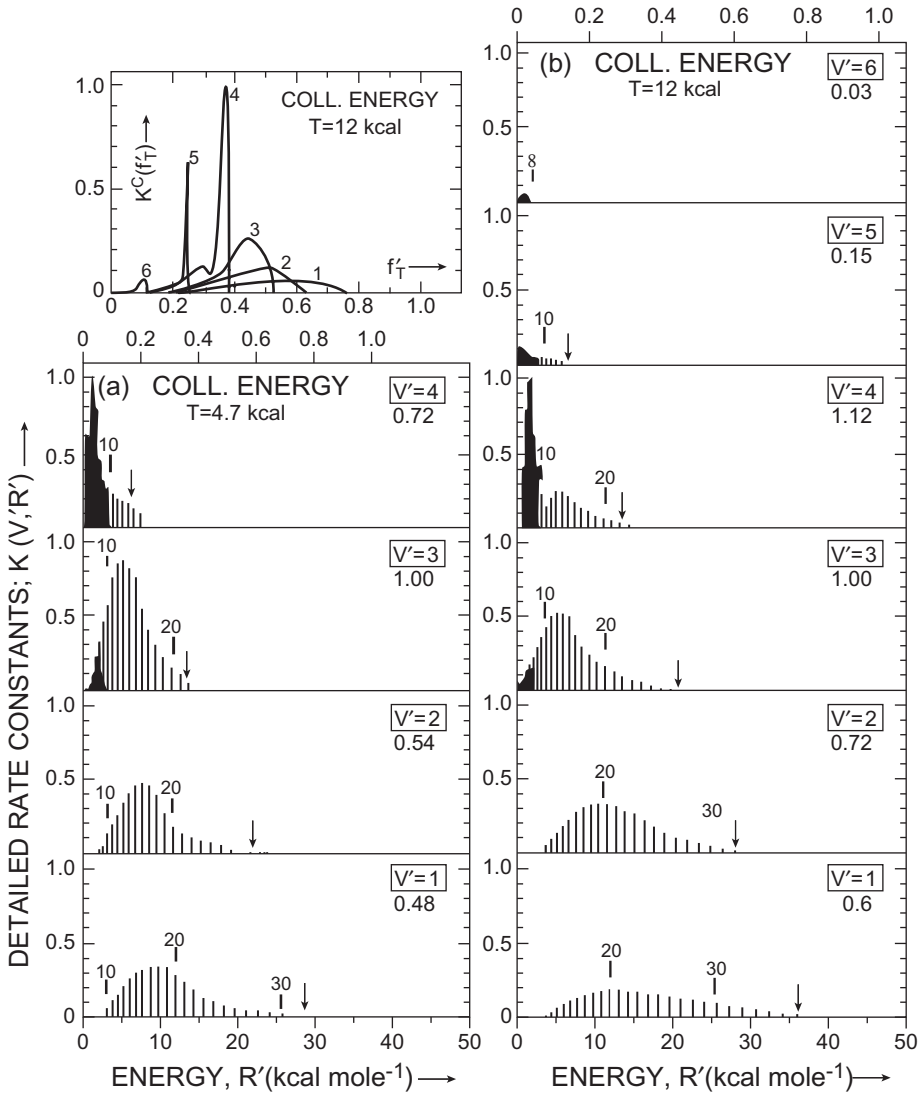

Fig. 1. Detailed rate constants, $k(V',R')$, versus product rotational energy within the specified vibrational energy levels, v'; (a) at a mean collision energy of $T = 4.7$ kcal mole^{-1}, and (b) at $T = 12$ kcal mole^{-1}. The scale at the top (0–1.0) gives the fraction of the total available energy [E'_{tot} from Eq. (1) is 37.1 kcal for (a), 44.4 kcal for (b)] going into rotation in a given v'-level. Values of $k(v')$ are given below the v' designation. Numbers above the vertical lines indicate J': the arrows indicate the (mean) energy available for rotational excitation in each v' level, from Eq. (1). The inset shows the continuum detailed rate constant $k^c(f'_T)$ (Ref. [4]) versus the fraction of the available energy going into product translation, f'_T at $T = 12$ kcal mole^{-1}; the vibrational levels to which the translational distributions refer are indicated above the curves.

ture behaved as an ideal gas [8]. Specific heats, molecular weights and collision cross sections were taken as mole-fraction averages. For experiments 1–5 the ratio of specific heats weighted by mole-fraction gave $\bar{\gamma} = (\sum X_i C_{pi} / \sum X_i C_{vi} =) 1.43, 1.34, 1.33, 1.34$ and 1.52 for the Cl_2 jet. The corresponding Mach numbers were approximately 5, 10, 13, 8 and 7. At our oven temperatures and pressures the formation of Cl_2 by recombination in the expanding jet should be slight [9].

The oven assembly was supported by copper pipes from a glass flange at the top of the vessel. These pipes circulated cooling water (separately) through copper blocks at either end of the graphite rod, which was soft-soldered into the blocks. The cooling pipes also

acted as electrical conductors for the heating current. Oven temperature was determined pyrometrically. To minimise thermal IR emission the hot oven, mounted out of view of the spectrometer, was surrounded by a water-cooled radiation shield. Strips of blackened copper sheet, extending $\frac{1}{4}''$ out from the wall at $\frac{1}{4}''$ intervals, were soldered to the blackened inner walls of the liquid-nitrogen-cooled can [6].

With the exception of the inlet system, apparatuses 1 and 2 (Table 1) were those described previously [6]. Infrared emission was recorded on a Perkin Elmer 112G grating spectrometer, using a PbS detector at −196 °C. The analysis of the spectrum to yield populations has been described [10]. Both gases were obtained from Matheson of Canada, and were vacuum distilled twice, to remove traces of air that would oxidise hot graphite.

2. Results and discussion

The observed rotational distributions showed an initial peak at higher-J' and a relaxed (Boltzmann) peak [1,6]. The latter was folded back into the former by the truncation method [6], tested in Ref. [11]. The corrected initial distributions for $T = 4.7$ and $T = 12$ kcal mole^{-1} are shown in Fig. 1. It is clear.

(a) that the vibrational distribution is broader at the higher collision energy,
(b) that the rotational distributions at $T = 4.7$ kcal mole^{-1} and $T = 12$ kcal mole^{-1} tend to populate J' levels up to the respective thermodynamic limits, and
(c) that there is a second peak in the rotational distribution in level $v' = 4$ at the higher collision energy.

The broadening of the vibrational distribution is clearly evident in Fig. 2, which includes thermal data ($T \approx 1.5$ kcal mole^{-1}) [2,4,12], as well as data at $T = 4.7$, 6 and 12 kcal mole^{-1}. This broadening in vibrational distribution produces at first a decrease and then an increase in mean vibrational excitation, $\overline{V}'$ [Fig. 3(a)]. The

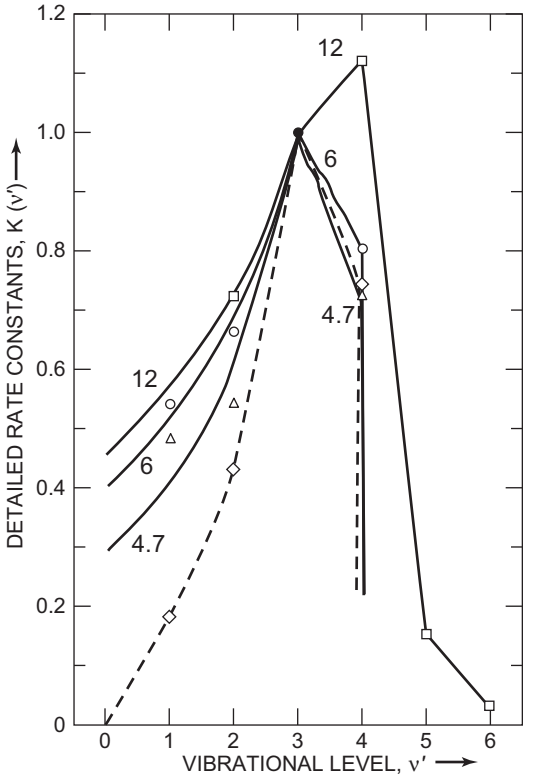

Fig. 2. Detailed rate constants, $k(v')$, versus v' from the present experiments at mean collision energies $T = 4.7(\Delta)$, $6(\circ)$, and 12 kcal mole^{-1} $(\square)$, and from earlier work [1–4,12] at $T \approx 1.5$ kcal mole^{-1} (broken line, $\diamond$). The $T = 6$ kcal data is the mean of results from experiments 2 and 3 using two jets, and experiment 4 using one jet (see text); the individual values, in the same sequence, were $k(v' = 1) =$ –, 0.61, 0.48; $k(v' = 2) = 0.53$, 0.79, 0.67; $k(v' = 3) = 1.00$; $k(v' = 4) = 0.74$, 0.67, 0.98. For $T = 1.5 - 6$ kcal mole^{-1} the populations in $v' = 5$ and 6 were below the Level of detection.

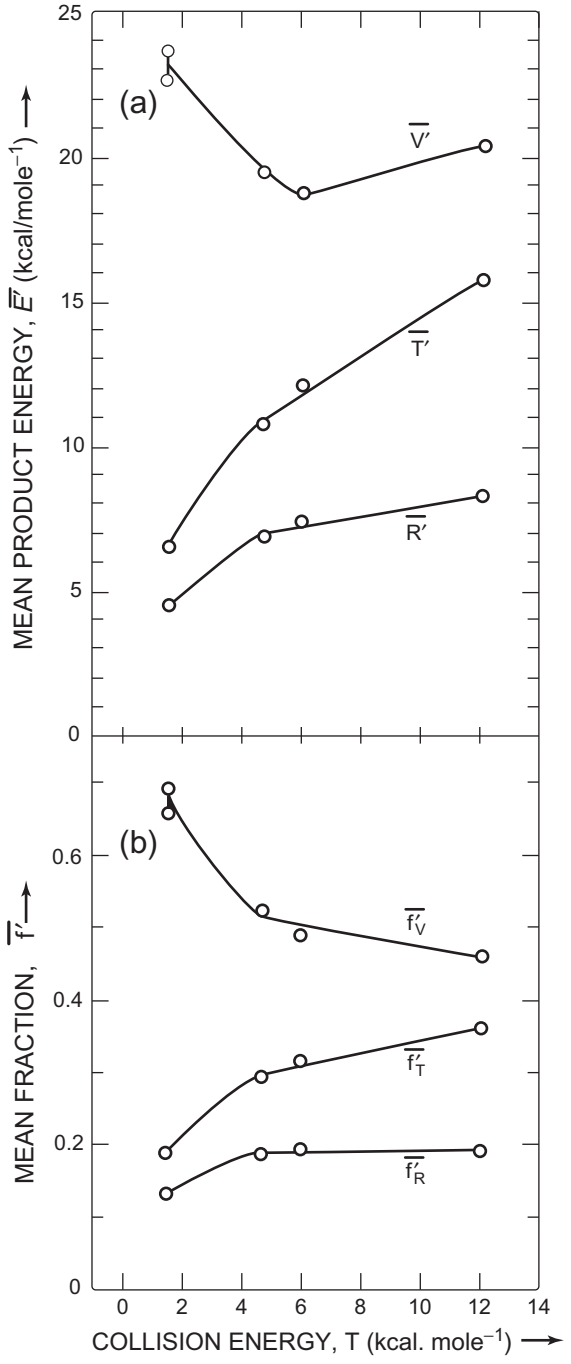

Fig. 3. (a) Mean product energies (averaged over all products) as a function of collision energy T. (b) Mean fraction of E'_{tot} in product vibration, rotation and translation $(\bar{f}'_V, \bar{f}'_R, \bar{f}'_T)$ as a function of T. The data at $T = 1.5$ kcal in (a) and (b) is from earlier work [1–4,12]; the upper points for $\overline{V}'$ and $\bar{f}'_V$ at $T = 1.5$ kcal assume $k(v' = 0) = 0$, the lower points assume $k(v' = 0) = 0.1$ (compare Fig. 2). The circles for $T = 4.7 - 12$ kcal are large enough to encompass the effect on $\overline{T}', \overline{R}', \bar{f}'_T$ and $\bar{f}'_R$ of varying the peak of the assumed rotational distribution in $v' = 0$ from $(\bar{J}')_{v'=0} = 20 [= (\bar{J}')_{v'=1}]$ to $(\bar{J}')_{v'=0} = 24$ [obtained by extrapolation from $(\bar{J}')_{v'>0}$].

total energy, E'_{tot}, is increasing sufficiently rapidly that the mean fraction entering vibration, $\bar{f}'_V$, is steadily decreasing [Fig. 3(b)].

The tendency to populate higher J'-levels in lower v'-levels is particularly characteristic of Cl + HI (cf. H + Cl_2 [3] and F + H_2 [5]). The novel observation [(b) above] is that J'_{max}, the highest J'-level populated in a given v'-level, increases with the new variable, T, so that rotational levels up to the thermodynamic limit continue to be populated. The most-populated J'-level, $\hat{J}'$, in a particular v'-level, remains almost invariant with T. The modest increase in $\overline{R}'$ with T, recorded in Fig. 3(a), is largely due to the increase in J'_{max} (in all v'-levels).

Energy that does not go into product vibration or rotation must go into translation. Much the largest increase in product energy, as the collision energy is increased, is in $\overline{T}'$, which rises by 9.5 kcal mole^{-1} a.s the collision energy increases by 10.5 kcal mole^{-1} [Fig. 3(a)]. This represents a significant increase in $\bar{f}'_T$, from 0.19 to 0.36 [Fig. 3(b)]. We have included the distribution over f'_T for our highest collision energy, in the inset to Fig. 1.

The third point evident from Fig. 1 was the emergence of a new peak in R' of $v' = 4$ (see also the inset to Fig. 1). There was a suggestion of this second peak in R' of $v' = 4$ at $T = 4$ kcal mole^{-1}, and clear evidence of it in all three experiments at $T \approx 6$ kcal mole^{-1}. Doubling of the collision energy ($T = 6$ to 12 kcal) produced no significant shift in the position of the maximum of this new rotational peak ($\hat{J}' = 13$), though it caused a substantial extension in the high-energy tail of the distribution.[2] The location of the maximum may be determined by the existence of a fairly well-defined second path across the potential-energy hypersurface. This could be a route which involves a high impact-parameter collision of Cl with I, followed by migration of Cl from the I end of HI to the H end [→ HCl + I ($^2P_{3/2}$)]. Alternatively the new reaction path could involve crossing onto the surface leading to HCl + I*($^2P_{1/2}$), followed by reversion to the lower surface[3] [6]. Crossing may be favoured by certain of the 6 initial states of Cl($^2P_{3/2}$, $M_J = \pm\frac{3}{2}, \frac{1}{2}$; $^2P_{1/2}$, $M_J = \pm\frac{1}{2}$) [13]. The tail of the rotational distribution, which is sensitive to T in all v', could well arise from the tendency for increased initial orbital angular momentum, L, to give rise to increased product rotational angular momentum J' (observed in trajectory calculations on a wide variety of surfaces).

Classical trajectory calculations employing a repulsive potential-energy surface for this reaction [2,14], performed previously, predicted that for an increase in T from thermal collision energy to 6 kcal mole^{-1};

(i) most of $T \rightarrow T'$,
(ii) the distribution over V' became broader,
(iii) there was a small decrease in $\overline{V}'$, and increase in $\overline{R}'$, and
(iv) angular-scattering of the HCl became sharply forward.

No evidence was found for the second rotational peak in $v' = 4$ (this failure is not instructive, since the statistics for $v' \approx 4$ were poor). These predictions are in quite good agreement with the present experiments as they relate to (i), (ii) and (iii), and with recent beam experiments regarding (i) and (iv) [15] (for Cl + HI see Ref. [16], for H + Cl_2 see Ref. [17]).

Taken together the chemiluminescence experiments [1–4] and beam experiments [15–17] show a markedly increased efficiency of conversion of the reaction energy into vibration and markedly enhanced tendency for forward scattering in the reaction Cl + HI → HCl + I as compared with H + Cl_2 → HCl + Cl. These differences appear to be due predominantly to the difference in the masses involved: for H + Cl_2 strong repulsion between the products throws HCl backward with high translational energy, for Cl + HI similar repulsion produces internal excitation. in the extended Cl–H ("mixed energy-release") and consequently Cl is able to continue in a forward direction carrying the H with it [2,18].

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[2] This second rotational peak is believed to be the result of direct reaction into $v' = 4$. Further experiments at higher collision energy are planned to check that this is the case. Preliminary data on the reaction H + ICl → HCl + I gave evidence of a multiply-peaked distribution (Ref. [4]); recent work (in progress) indicates that the peaks at lower J' in. this system may have been due to a secondary process rather than the primary reaction.

[3] The second rotational peak cannot arise from the reaction Cl + HI → HCl + I*($^2P_{1/2}$). At $T = 6$ kcal, for example, the formation of HCl ($v' = 4, J' = 13$) would be 20 kcal endothermic.